

## Philadelphia, October 1991

The Tantalum-Niobium International Study Center will hold a conference from October 23rd to 25th 1991 in Philadelphia, Pennsylvania, with the Thirty-second General Assembly on October 24th. The technical sessions and social events will be held at the Sheraton Society Hill Hotel, where rooms have been booked for the delegates to stay. The hotel, which has all the facilities expected of a modern conference venue, is situated in the historic area of the city, with shopping and restaurants nearby.

On October 23rd the T.I.C.'s registration desk will be open for the distribution of conference papers, and on the evening of that day everyone is invited to a reception to welcome all the delegates and guests and their ladies. Following the General Assembly on the morning of Thursday October 24th there will be a programme of technical presentations focusing on processing and on end uses of niobium and tantalum.

Cabot Corporation and Showa Cabot Supermetals will generously host the reception and dinner which will close the day's events. On October 25th there will be a plant tour of Cabot Corporation's facilities at Boyertown, and an alternative tour of Carpenter Technology at Reading.

Ladies' tours of particular interest to such an international gathering as is usual for our meetings are being arranged.

### TECHNICAL PROGRAMME

Papers will focus on the processing of niobium and tantalum and on end uses for the metals: presentations are expected to include the following:

#### **New developments in capacitor products for high specific capacitance and high voltage applications,**

Dr H. Chang, Cabot Corporation Electronic Materials & Refractory Metals Division

#### **Trends of chip-type capacitors in Japan,**

Mr Hiroshi Adachi, Hitachi AIC Inc.

#### **New opportunities for growth in tantalum capacitors,**

Mr William Millman, AVX Ltd., Tantalum Division

#### **Application of tantalum and niobium in oxide capacitor manufacturing,**

Mr Y.M. Mudrolubov, Vicon, Positron (Leningrad)

#### **Research in the field of metal oxide physics,**

Dr S.D. Khanin, Vicon, Positron (Leningrad)

#### **Developments in Cu-Nb and Cu-Ta composite materials,**

Dr William A. Spitzig, Ames Laboratory

#### **Characteristics of capacitor grade tantalum powder in relation to the pore size distribution of the sintered body,**

Mr Y. Mizusaki, Showa Cabot Supermetals

#### **Refractory metals requirements for high-explosive ordnance,**

Dr Joseph Carleone, Aerojet Electronic Systems Division

#### **The role of niobium and tantalum in superalloys,**

Dr P. Kumar, Cabot Corporation Electronic Materials & Refractory Metals Division

## European Metals Conference

The T.I.C. will take part in the exhibition of EMC'91, being held at the Hilton Hotel in Brussels from September 15th to 20th 1991. The conference organisers are Benelux Metallurgie, Gesellschaft Deutscher Metallhütten und Bergleute and The Institution of Mining and Metallurgy.

## President's letter

I write this letter as the civilised World heaves a great sigh of relief at the outcome of the attempted coup in the Soviet Union. A renewed descent into the confrontations and stagnation of the past was mercifully halted, and the gloom generated by this spectre is lifting once again.

Hopefully these recent events will reinforce the power and the will to restructure and restart the economies of those countries previously labouring under centralist dogma. The Western World could certainly do with a further stimulus for the recovery from recession, and our own industries will surely benefit from that.

In a few weeks we will meet at the General Assembly in Philadelphia. The emphasis on the downstream of this year's papers will I'm sure be of great interest to us all. It is vital for our future to understand the directions in which our products are moving today. I look forward to seeing you there.

Peter Adams  
President  
23rd August 1991

## Titanium conference

The Seventh International Meeting on Titanium will be held on November 15th 1991 in Turin, Italy, from 10a.m. to 18.30p.m. The conference is being organised by Ginatta Torino Titanium and information may be obtained from Ms Carita Loro, Conference Secretariat, GTT, Via Brofferio 3, 10121 Torino, Italy.

## Tantalum in Venezuela

At the T.I.C. General Assembly held in Rio de Janeiro in October 1988 we heard an interesting talk by Dr Simon Rodriguez, then Director of the Geological Survey of Venezuela, on some significant mineral deposits of tantalum-tin-niobium discovered in the south-west of the country, near the Colombian border. Dr Rodriguez is now the coordinator of the International Geological Correlation Program for Venezuela, and he has kindly sent us the following report on the latest developments relating to tantalum recovery in that country.

### INTRODUCTION

A large granitic province of Venezuela, located in the western-most part of Bolívar State, has shown an important Ta-Sn-Nb mineralization. Studies done by the Geological Survey of Venezuela, Ministry of Energy and Mines, between 1975 and 1986 over an extensive zone of Western Bolívar showed the presence of numerous large complex pegmatites affecting a non-tectonized sequence of granites and sienites. The pegmatitic bodies are rich in thick extensive quartz veins intruding the mother rock. Detailed economic investigations, which included remote sensing, lithologic mapping, mineralogy and preliminary evaluation work, determined the existence of cassiterite-tantalite-rare metals-rutile mineralization associated mainly with the quartz veins and the quartz-rich pegmatites. Secondary eluvial levels located near the pegmatite bodies showed high concentrations of Ta-Sn-Nb minerals (figure 1).

## T.I.C. statistics

### TANTALUM

#### PRIMARY PRODUCTION

(quoted in lb Ta<sub>2</sub>O<sub>5</sub> contained)

	2nd quarter 1991
Tin slag (2 % Ta <sub>2</sub> O <sub>5</sub> and over)	218 957
Tantalite (all grades), other	206 839
<b>Total</b>	<b>425 796</b>

Note : 17 companies were asked to report, 16 replied. The companies which reported included the following, whose reports are essential before the data may be released :

Datuk Keramat Smelting, Greenbushes, Malaysia Smelting, Mamoré Mineração e Metalurgia, Metallurg group, Pan West Tantalum (Wodgina Mine production), Tantalum Mining Corporation of Canada, Thailand Smelting and Refining

#### QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta<sub>2</sub>O<sub>5</sub> contained)

LMB quotation :	US \$ 30	US \$ 40	US \$ 50
3rd quarter 1991	240 800	330 100	355 500
4th quarter 1991	245 800	330 100	355 500
1st quarter 1992	255 800	346 100	371 500
2nd quarter 1992	255 800	348 100	371 500
3rd quarter 1992	260 800	348 100	371 500

Note :

The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

#### PROCESSORS' RECEIPTS

(quoted in lb Ta contained)

	2nd quarter 1991
Primary raw materials (e.g. tantalite, columbite, struverite, tin slag, synthetic concentrates)	253 047
Secondary materials (e.g. Ta <sub>2</sub> O <sub>5</sub> , K <sub>2</sub> TaF <sub>7</sub> , scrap)	88 584
<b>Total</b>	<b>341 631</b>

Note : 14 companies were asked to report, all 14 replied.

#### PROCESSORS' SHIPMENTS

(quoted in lb Ta contained)

Product category	2nd quarter 1991
Ta <sub>2</sub> O <sub>5</sub> , K <sub>2</sub> TaF <sub>7</sub>	24 370
Alloy additive (& scrap) *	37 566
Carbides	96 701
Powder/anodes	220 457
Mill products	94 523
Ingot, unwrought metal, other (& scrap) *	40 812
<b>Total</b>	<b>514 429</b>

equivalent to 694 479 lb Ta<sub>2</sub>O<sub>5</sub>.

Notes :

\* Categories were combined in accordance with the rules of confidentiality : in April and June "scrap" was combined with "ingot, unwrought metal and other", and in May "scrap" was combined with "alloy additive".

14 companies were asked to report, and all 14 replied. For both receipts and shipments by processors, reports by the following companies are essential before the data may be released :

Cabot Corporation, Electronic Materials and Refractory Metals, W.C. Heraeus, Kennametal, Metallurg Group, Mitsui Mining and Smelting, NRC Inc., Showa Cabot Supermetals, Hermann C. Starck Berlin, Treibacher Chemische Werke, Vacuum Metallurgical Company, V Tech

### NIOBIUM

#### PRIMARY PRODUCTION

(quoted in lb Nb<sub>2</sub>O<sub>5</sub> contained)

	2nd quarter 1991
Concentrates : columbite, pyrochlore	10 605 960
Occurring with tantalum : tin slag (over 2 % Ta <sub>2</sub> O <sub>5</sub> ), tantalite, other	229 660
<b>Total</b>	<b>10 835 620</b>

Note :

18 companies were asked to report, 17 replied. The companies which reported included the following, whose reports are essential before the data may be released : Cambior, Mineração Catalao de Goiás, Niobium Products Co. (CBMM)

#### PROCESSORS' SHIPMENTS

(quoted in lb Nb contained)

	2nd quarter 1991
Compounds and alloy additive : chemical and unwrought forms (e.g. NbCl <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> , NiNb, FeNb [excluding HSLA grades])	830 305
Wrought niobium and its alloys in the form of mill products, powder, ingot and scrap	
(i) Pure niobium	56 979
(ii) Niobium alloys (such as NbZr, NbTi and NbCu)	83 071
HSLA grade FeNb	6 938 289
<b>Total</b>	<b>7 908 644</b>

Note : 15 companies were asked to report for the first quarter 1991, all 15 replied. Reports by the following companies are essential before the data may be released : Cabot Corporation, Electronic Materials and Refractory Metals, Greenbushes, W.C. Heraeus, Kennametal, Metallurg Group, Mitsui Mining and Smelting, Niobium Products Co. (CBMM), NRC Inc., Hermann C. Starck Berlin, Teledyne Wah Chang Albany, Treibacher Chemische Werke, Vacuum Metallurgical Company

## Capacitor statistics

### U.S. TANTALUM CAPACITOR SALES

(thousands of units)

#### 1st quarter 1991

Metal-cased	19 842
Moulded	67 518
Dipped	90 894
Chips	111 632
Wet slug	1 730
<b>Total</b>	<b>291 616</b>

Foil : not included.

(Data from EIA)

### EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

#### 1st quarter 1991

	190 576
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(Data from ECTSP)

### JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

#### 1st quarter 1991

Production	1 101 326
of which exports	250 239

(Data from JEIDA)



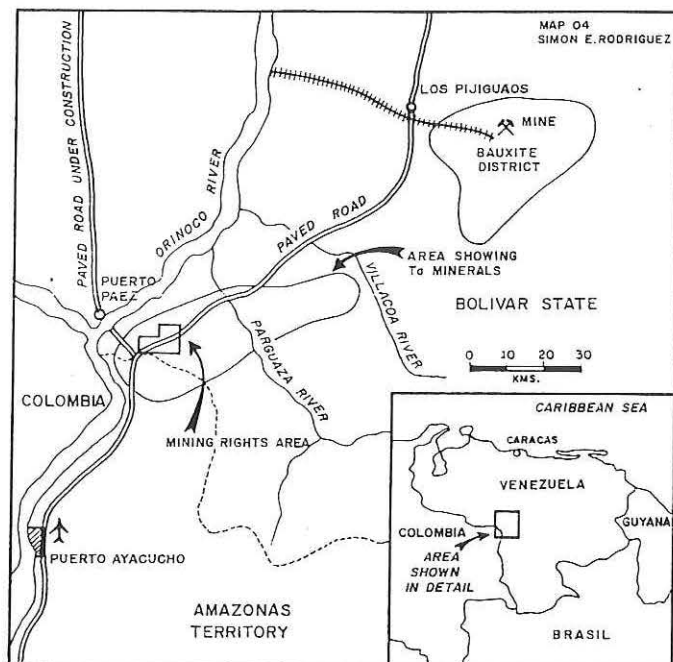


Fig. 1 : Tantalum district of south western Venezuela

## CURRENT STATUS

During 1989 and 1990 a large northern area (the subject of a preliminary study by the Geological Survey) located between the Parguaza and the Orinoco rivers, was under investigation by the Venezuelan private sector in order to outline favourable zones for future developments.

The preliminary exploration work, authorized by the Ministry of Energy and Mines, included detailed sampling, outlining of pegmatite bodies, geological contacts, local tectonic patterns, location of quartz veins and general geological mapping. Typical samples of tantalum ore were sent to several international consumers so that they could examine the material.

As a result of this work several important eluvial zones were detected and provisionally outlined. The ore zones are characterized by levels of tantalite-rich sediments interbedded with clays, laterite material and quartz gravels. The economic zones were located quite near to pegmatite and quartz vein outcrops. Fine sediments located far from those outcrops showed a poor concentration of Ta-Sn-Nb minerals; only ilmenite, magnetite and zircon were detected. Paved roads are located quite near the studied zones.

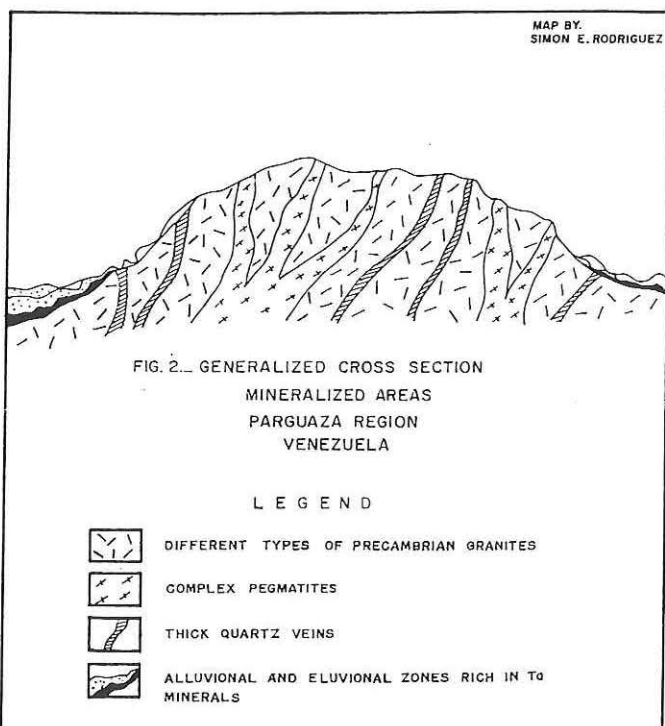


Fig. 2 : Cross section

The morphological and lithological parameters of those secondary eluvial levels support the application of intensive open pit local mining using conventional mobile concentrating tables in order to produce a final high grade tantalite ore. Normally the ore of the Parguaza Ta-Sn-Nb district shows a  $Ta_2O_5$  content ranging between 25 and 42 per cent.

Several Venezuelan ferroalloy companies, manufacturing mining equipment firms and important engineering consulting offices have already applied for large mining permits to the Ministry of Energy and Mines. More than 100 square kilometres, covering mainly pegmatites and eluvial-rich zones, have already been solicited for future mining, but there is still a large area showing tantalum-rich potential sequences in the region (figure 2).

If those grants are approved by the Ministry of Energy and Mines during 1991, quite possibly open pit mining will start during the third quarter of 1992, after the detailed evaluation of the main areas.

## The world's principal tantalum and niobium mines

All the world's major tantalum and niobium mines were working close to capacity by the end of 1990, so this seems a good opportunity to review their present status, at a time of reasonable market stability.

### NIOBIUM

1. The world's largest producer of niobium is the CBMM mine at Araxá in Minas Gerais state in Brazil. The huge deposit of pyrochlore being worked there was discovered by Professor Guimaraes in 1954, and its reserves of some 8.2 million tons of contained metal are sufficient for 500 years at the present rate of consumption. The CBMM set up to operate the mine is owned 55 % by Grupo Moreira Salles and 45 % by Molycorp.

The company processes its mine concentrates on site, with furnaces for production of ferroniobium (both HSLA for steelmaking and high-grade for superalloys) and chemical plant and vacuum furnaces for the production of niobium metal and oxide. During 1990 its output of ferroniobium (67 % Nb) was 13 100 tons, while its pure oxide plant produced 1472 tons  $Nb_2O_5$ . Niobium metal and high grade alloys totalled 300 tons. Construction of a new ferroniobium unit was announced during 1990 : it will have a capacity of 22 800 tons per year, and it is due to come into operation in 1992.

2. Also in Brazil is the mine and smelter of Mineração Catalão de Goiás (a member of the Anglo-American Group), situated at Catalão in Goiás state. All the pyrochlore produced by the mine is converted to HSLA grade ferroniobium in house, and in 1990 production was 3250 tons : output in 1991 is forecast at around 3130 tons, reflecting a continuing fall in world demand for crude steels, offset to some extent by relative strength of demand for specialty steels.

3. The Canadian niobium producer is the Niobec Mine at St. Honoré, Quebec, jointly owned by the Teck Corporation of Vancouver, which operates the facilities, and Cambior Inc., of Val d'Or, which markets the pyrochlore concentrates. The deposit was discovered in 1967 by a survey exploring for uranium : the mine was brought into production in 1975. Whereas the Brazilian mines are open-cast, this mine uses underground methods, operating to a depth of 300 metres. The concentrates, containing around 60 %  $Nb_2O_5$  are sold principally to converters in the United States, England and Japan for the production of ferroniobium. During 1990 output totalled 3390 tons of  $Nb_2O_5$  contained (sufficient to produce 3320 tons of ferroniobium) : that for 1991 is expected to be somewhat lower, due to changes in the characteristics of the ore being mined.

### TANTALUM

1. The Greenbushes mine (owned by Gwalia Consolidated Ltd.) is situated in southern Western Australia and the area has a long history of metal mining (there was a tin smelter there a hundred years ago). It started life in its present form in 1964 predominantly as a tin mine, switching to tantalum in significant quantities only in the early 1970's when demand for the metal took off with the development of the tantalum capacitor. By 1980 the company had proved a hard rock tantalite below the existing workings; recently they have announced that they plan to work this by deepening the current open-cast tantalum pit, and this would bring their initial annual output of tantalite to 295 tons.

In 1990 production was 269 760 pounds contained  $Ta_2O_5$ , lower than previously, and reflecting the weakness of the market early in the year. In January this year they announced the signing of long term

contracts for the sale over the next five years of 1.3 million pounds of contained Ta<sub>2</sub>O<sub>5</sub> at fixed prices in U.S. dollars : production in 1991 will be raised to 360 000lbs Ta<sub>2</sub>O<sub>5</sub> to meet these commitments.

2. Wodgina, in the Pilbara district of Western Australia, has been the site of tin, tantalum, and beryl mining ever since the discovery in 1902 of the pegmatite bodies there. Mining for tantalum has been more or less continuous in the area since 1905. Full scale development followed prospecting in 1987/88 by the owners Pan West Tantalum (jointly owned by Pancontinental and Goldrim). The concentrator was commissioned in November 1989 and the first shipment of tantalum concentrates (mostly wodginite, but with some microlite) was made in February 1990. Production in the year was 282 000lbs contained Ta<sub>2</sub>O<sub>5</sub> and the target for this year is 200 000lbs. The present deposit will be worked out around 1994, after which they expect to turn their attention to the satellite orebodies at Mt. Cassiterite and Tabba Tabba. These contain between them 2.2 million lbs Ta<sub>2</sub>O<sub>5</sub> and so could extend the project life by up to ten years.

3. The pegmatite at Bernic Lake in Manitoba, Canada was discovered in 1929 and was for a short while worked for tin, and again, briefly, in the 1950's for lithium, but since 1969 it has been mined by the Tantalum Mining Corporation (TANCO - now owned 37.5 % by Hudson Bay, 37.5 % by Cabot and 25 % by the Manitoba government) for its caesium, lithium, rubidium, and tantalum.

Production of tantalum was suspended from 1982 to 1988, but its mill was successfully adapted by the company to enable it to get into the spodumene business (which now has its own dedicated plant).

In 1990, following the purchase and installation underground of new lift and drilling equipment, they were able to start reducing the number of pillars, all containing high grade tantalum, and this had the effect of adding some seven years to the reserves at the mine. In the summer months they are also able to reprocess tailings (of which 25 000 tons were put through the mill last year). Production of tantalite was 230 000lbs contained Ta<sub>2</sub>O<sub>5</sub>, and this is expected to be repeated in 1991.

It is a curious coincidence that the markets for the two metals in our center's title are each fed from three major mines in the world, with two of the mines in one country (Brazil for niobium, Australia for tantalum) and the third in Canada. Perhaps the geologists have an answer !

R.J. Tolley  
Technical Adviser

## The technology of tantalum carbide

By Dr Erich Schaschel, Treibacher Chemische Werke A.G., presented at the meeting of the T.I.C. held in Perth in November 1990.

### INTRODUCTION

TaC has gained technological significance closely linked to the development of hardmetals. Only by alloying WC + Co hardmetals with TaC and TiC could their superiority to high speed steels for cutting applications be realized. As a refractory metallic hard material with exceptionally high hot hardness, good corrosion resistance and other special properties, TaC became an essential component for most hardmetal grades (1).

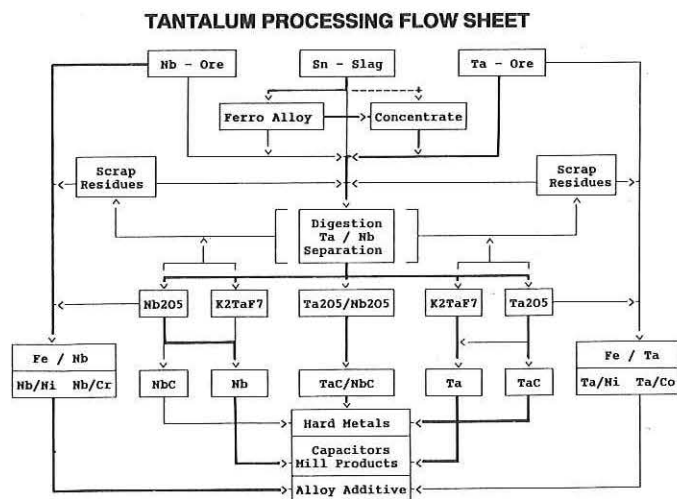
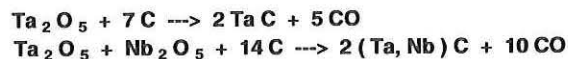


Fig. 1 : Tantalum processing flow sheet

**A**



**B**



**C**



**D**



**E**



Table 1 : Production methods for TaC and TaC/NbC

In the processing flow chart of Ta (Fig. 1) one can see that TaC and (Ta,Nb)C are located in important lines. Raw materials are Ta-Nb-containing ore concentrates, Sn-slugs, scrap and different residues. These raw materials are digested either directly with hydrofluoric acid or first concentrated by a separate process. Separation and purification of the Ta-Nb-F-salts is carried out by a liquid/liquid extraction process with methyl isobutyl ketone (2). The oxides are reacted with carbon to produce the carbides.

### PRODUCTION METHODS

Table 1 shows different production methods for TaC and TaC/NbC (3).

**Method A** is the standard production method; B, C, D and E are less important and may be used under special conditions. Basic starting materials for a production process according to method A are the oxides, either pure or as mixtures. They are mixed with carbon black and reacted in inert atmosphere or vacuum at temperatures between 1400° and 1800 °C. The reaction is endothermic and controlled by the transport of C to the oxide and the removal of the resulting CO-gas. In case of oxide mixtures mixed crystals of (Ta,Nb)C are formed.

**Method B** is applied when the raw material is pure Ta-metal scrap. In order to facilitate the comminution the metal can be hydrided to TaH. This brittle compound is milled to a powder and mixed with carbon black. The reaction with carbon is exothermic and the temperature increase with the onset of the reaction at the beginning of the heating cycle has to be carefully controlled.

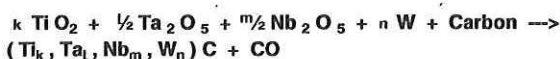
**Method C** is analogous to B but uses liquid metal such as Fe or Al as reaction promoting medium. This process is called the auxiliary metal bath process or the "menstruum process". Of great importance is the fact that the menstruum method permits the formation of solid solutions of TaC with other hard carbides of a completely homogeneous composition and in equilibrium. Problems yet to be economically solved are the isolation of the hard materials from the auxiliary metal. The carbides from this process are distinguished by very low O and N contents and by a uniform grain size and well developed crystal faces.

**Process D** is a combination of A and B. The presence of Ta accelerates the reaction.

**Method E** is a gas phase reaction and offers the possibility of producing very fine TaC powder.

The oxide method, with slight variations, is generally also applied for the synthesis of more complex mixed carbides that typically contain TaC and NbC besides WC and TiC.

**A**



**B**



Table 2 : Production methods for mixed carbides

Table 2, **method A** shows a typical oxide reaction formula (k, l, m and n are the mole fractions and determine the composition of the mixed crystal). The reaction temperature is in excess of 1800 °C in order to accelerate the reaction and to ensure a complete carbide solid solution to a homogeneous mixed crystal.

The **method B** starts from prefabricated carbides. The stoichiometry is easier to control. Yet the products are generally inferior in regard to a homogeneous composition of the mixed crystals and it is more difficult to obtain small particle sizes with narrow size distribution.

Fig. 2 shows production furnaces for TaC and mixed carbides.



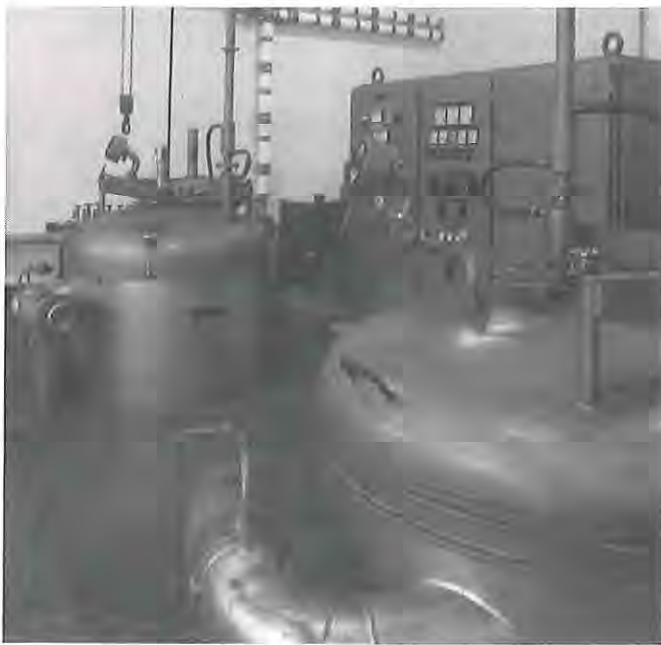


Fig. 2 : Production furnaces for TaC and mixed carbides

### PROPERTIES, SPECIFICATIONS AND QUALITY CONTROL

All metallic carbides of transition metals of groups IVb, Vb and VIb of the periodic table belong to the family of interstitial alloys. The term "interstitial alloy" should imply the fact that they have metallic character and simple metal-like structures. The carbon atoms occupy the

CARBIDE	GROUP	MICRO-HARDNESS	MELTING POINT °C	MODULUS OF ELASTICITY N/mm <sup>2</sup>	THERMAL CONDUCT. W/(m.K)	CRYSTAL STRUCTURE	LATTICE CONSTANTS, nm		
							a	b	c
TiC	IV b	3200	3067	451000	21	fcc	0,43278	---	---
ZrC		2560	3445	348000	38	fcc	0,46976	---	---
HfC		2500	3928	352000	29	fcc	0,46385	---	---
VC	V b	2900	2648	422000	39	fcc	0,41656	---	---
NbC		2100	3613	338000	18	fcc	0,44702	---	---
TaC		1550	3985	285000	22	fcc	0,44555	---	---
Cr <sub>3</sub> C <sub>2</sub>	VI b	2150	1810	373000	19	orthorhombic	0,55274	0,28289	1,14838
Mo <sub>2</sub> C		1660	2517	533000	32	hexagonal	0,3002	---	0,4729
WC		2350	2776	696000	121	hexagonal	0,29060	---	0,28371

Table 3 : Properties of transition metal carbides of groups IVb, Vb and VIb

interstitial sites between the bigger metal atoms. Table 3 shows properties of the most important single carbides of this class (4, 5). All these carbides are refractory hard compounds characterized by high values of micro hardness, high melting points and high moduli of elasticity. The carbides of group IVb and Vb have cubic crystal structure with similar lattice parameters, but Cr<sub>3</sub>C<sub>2</sub> in VIb is orthorhombic, Mo<sub>2</sub>C and WC are hexagonal. The cubic monocarbides of groups IVb and Vb are completely miscible except for ZrC-VC and HfC-VC. That means that Ta/Nb mixed carbides can be prepared as single phase solid solutions independent of the composition. WC has a limited solubility in the carbides of groups IVb and Vb, but does not dissolve any other carbide by itself.

Fig. 3 shows the phase distribution in the pseudoternary system WC-TiC-TaC. This system is especially important in the metallurgy of cemented carbides. In this phase diagram one can see that TiC is a better solvent for WC than TaC. TaC additions reduce the solvent power of TiC for WC. The maximum solubility of WC at a given temperature is in the pseudobinary system of WC/TiC and the least solubility in the WC/TaC-system. Compositions in the lower area form single phase solid solutions of mixed crystals; in the upper area two phases, free WC and the mixed crystal, coexist. The solubility of WC in TiC and TaC increases with increasing temperature.

Of the mechanical properties hardness and transverse rupture strength are of great importance. As can be seen in Fig. 4 these properties are influenced by the carbon content of the carbide. The hardness of TaC increases as the C-content decreases from the composition TaC to TaC<sub>0,85</sub>. The opposite effect can be seen for the transverse rupture strength (5).

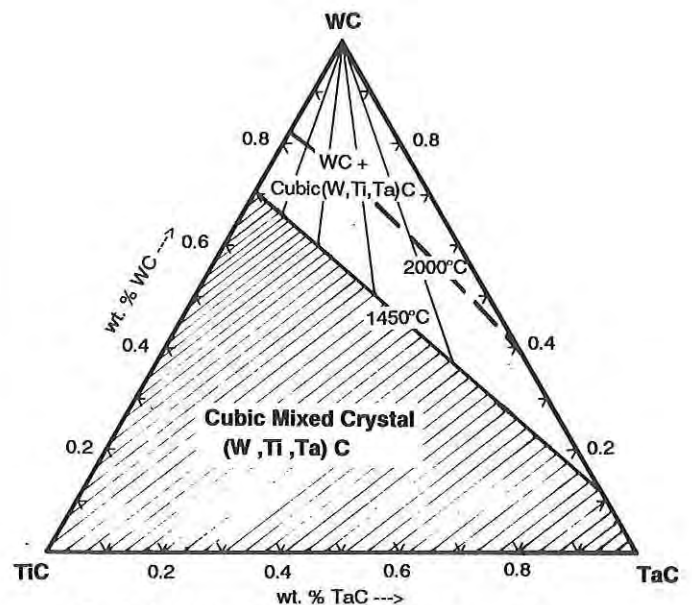


Fig. 3 : Isothermal section of the pseudoternary system WC-TiC-TaC at 1450°C and 2000°C

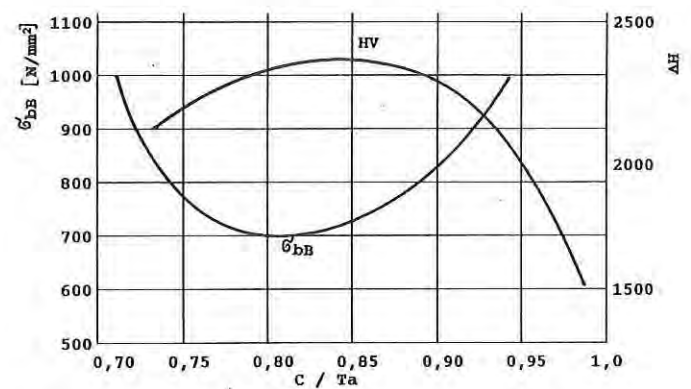


Fig. 4 : Micro hardness and transverse rupture strength of TaC

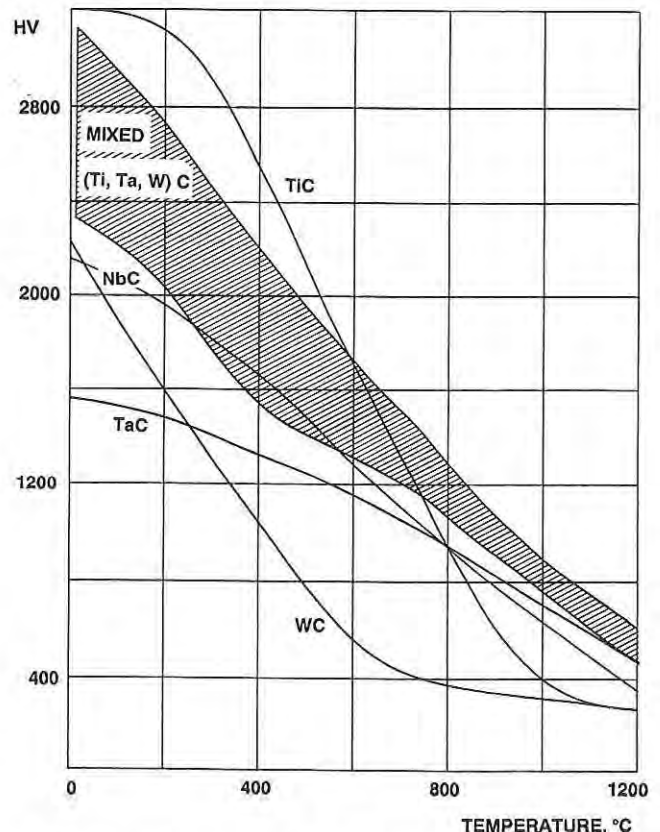


Fig. 5 : Hot hardness of WC, TiC, NbC and mixed carbides



Fig. 5 shows the hot hardness of TiC, TaC and mixed carbides and is based on a publication by Miyoshi and Hara (6). Newer data have also been incorporated (5). The hot hardness is a property that is important in cutting tool applications. The hardness decreases generally with increasing temperature. At high temperature Ta-containing mixed carbide solid solutions appear to be superior to the other carbides.

Weight %	TaC	TaC / NbC 90 / 10	TaC / NbC 77 / 23	TaC / NbC 60 / 40
Ta	> 93,4	84,1 ± 0,5	72,5 ± 0,5	56,2 ± 1,0
Nb	< 0,10	9,0 ± 0,5	20,0 ± 0,5	35,5 ± 1,0
C-total	6,25 ± 0,10	6,75 ± 0,15	7,35 ± 0,15	8,20 ± 0,15
C-free	< 0,15	< 0,15	< 0,15	< 0,15
O	0,10 - 0,25	0,10 - 0,25	0,10 - 0,30	0,10 - 0,30
N	< 0,02	< 0,02	< 0,03	< 0,04
S	< 0,005	< 0,005	< 0,005	< 0,005
Fe	< 0,02	< 0,02	< 0,02	< 0,02
Al	< 0,005	< 0,005	< 0,005	< 0,005
Si	< 0,005	< 0,005	< 0,005	< 0,005
Ca	< 0,005	< 0,005	< 0,005	< 0,005
Na	< 0,002	< 0,002	< 0,002	< 0,002
FSSS (microns)	0,8 - 2,0	0,8 - 2,0	0,8 - 2,0	0,8 - 2,0

Table 4 : Commercial grades of TaC/NbC

Table 4 shows the composition and main impurities and typical average particle sizes of commercial grades of TaC and TaC/NbC. Trends are towards lower limits of impurities and finer powders corresponding to developments in the hardmetal industry to micrograin grades requiring finer powders with narrow particle size distribution, without agglomerates, but consisting of stable grains.



Fig. 6 : SEM-images of commercial grades of TaC

Fig. 6 shows SEM images of four different grades of TaC. The picture in the right lower corner shows an old grade. The newer grades of TaC are finer with narrower particle size distribution.

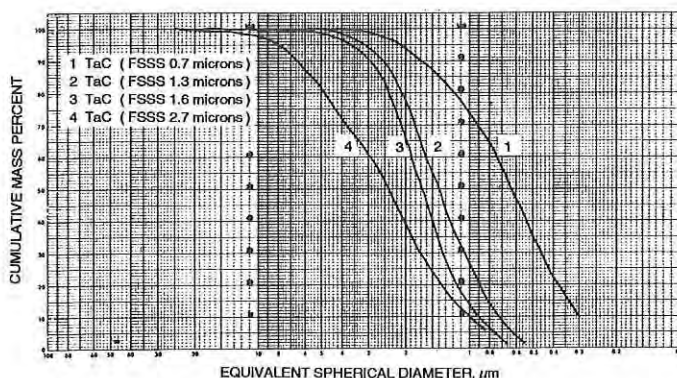


Fig. 7 : Particle size distribution of commercial grades of TaC

Fig. 7 shows the corresponding particle size distribution curves. The "old grade" no. 4 has a distinctly wider particle size distribution.

#### COMMERCIAL GRADES OF MIXED CRYSTALS

Weight %	WC/TaC 50/50	WC/TiC/TaC/NbC 33/33/25/8
W	46,5 ± 1,0	30,5 ± 0,5
Ti	—	26,5 ± 0,5
Ta	46,5 ± 1,0	23,6 ± 0,5
Nb	—	6,7 ± 0,2
C-total	> 6,10	> 10,8
C-free	< 0,15	< 0,15
O	0,10 - 0,30	0,10 - 0,35
N	< 0,02	< 0,04
S	< 0,003	< 0,003
Fe	< 0,05	< 0,06
Al	< 0,005	< 0,005
Si	< 0,005	< 0,005
Ca	< 0,005	< 0,005
Na	< 0,002	< 0,002
FSSS (microns)	1,2 - 2,0	1,2 - 2,5

Table 5 : Commercial grades of mixed crystals

Table 5 shows the composition and main impurities of two commercial grades of mixed crystals containing WC and TaC, and WC, TiC, TaC and NbC. In analogy to TaC, specifications have shifted towards lower limits of impurities, finer powders, narrower particle size distribution and improved homogeneity of the solid solutions.

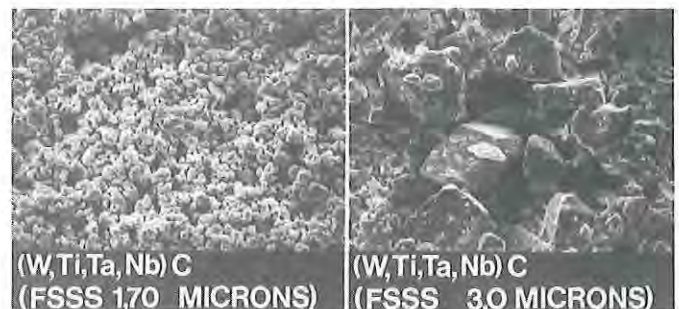


Fig. 8 : SEM-images of commercial grades of mixed crystals

Fig. 8 shows SEM images of two different grades of mixed crystals with identical composition demonstrating the development towards finer powder with very narrow particle size distribution.

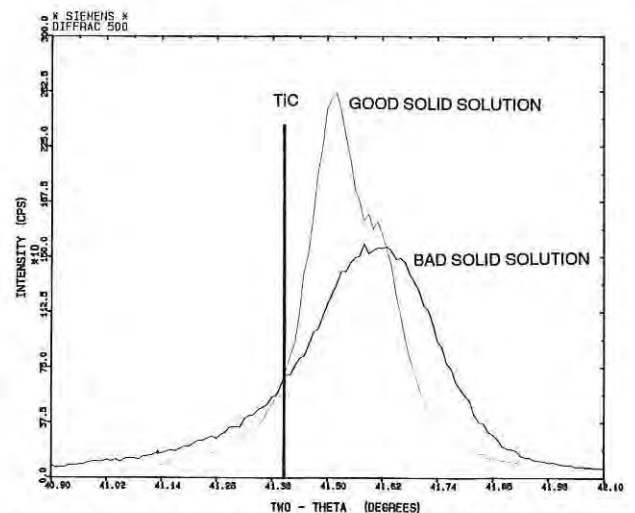
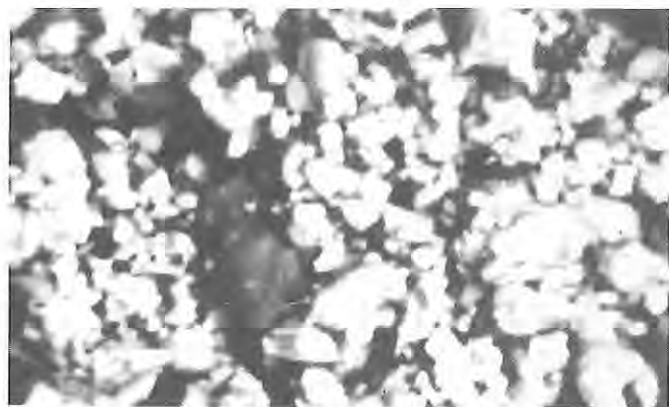


Fig. 9 : X-ray diffraction pattern of (W,Ti,Ta,Nb)C mixed crystals



Fig. 9 shows X-ray diffraction patterns of two WC/TiC-TaC/NbC mixed crystal grades that illustrate the improvement of homogeneity of carbide solid solution. The narrower X-ray diffraction lines indicate a more perfect homogeneous solid solution.



## (W, Ti, Ta, Nb) C MIXED CRYSTALS

Fig. 10 : SEM backscattering electron microscopy

Investigations of the mixed crystals for perfection of homogeneity and degree of solid solution can also be carried out by SEM. Fig. 10 shows a SEM image of a (W,Ti,Ta,Nb)C-mixed crystal by backscattered electrons. This SEM method allows an assessment of the quality of solid solution together with the particle size distribution. The mixed crystals on the SEM image appear bright, a free unreacted TiC particle appears dark. This method together with micro X-ray emission analysis can give very detailed information on the solid solution system of mixed crystals.

The final and ultimate quality control of carbide powders such as WC, TaC or mixed crystals is performed by a hardmetal test. The results are generally derived from the analysis of the micro-structure and from the physical and mechanical properties of a hardmetal test piece that is sintered under closely controlled conditions (7).

## APPLICATIONS AND SUBSTITUTION

The major application of TaC and Ta-containing carbide mixed crystals is in hardmetals.

Hardmetals are composite materials that consist of metallic hard carbides and cobalt metal as a binder. The combination of these two different types of components results in a unique material that is both very hard and also tough. WC is the basic hard component and TaC, NbC and TiC are additions with very special functions.

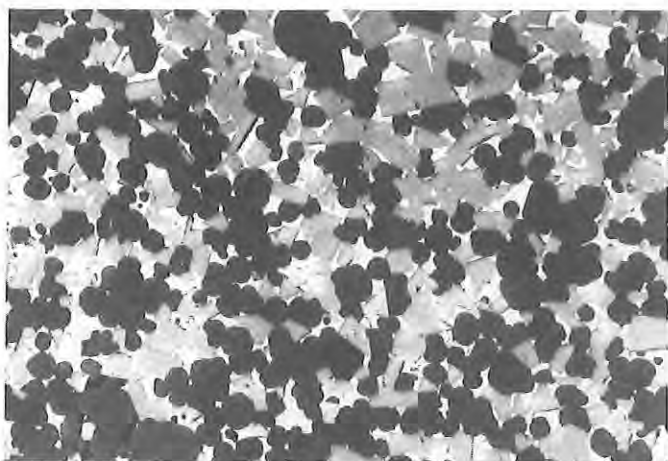


Fig. 11 : Microstructure of a WC-TiC-TaC-Co hard metal (photo-emission-electron-microscopy)

Fig. 11 shows the microstructure of such a hardmetal in a photo-emission-electron-microscope (8). The bright phase is Co, the light-gray phase of faceted grains is WC and the dark spherical grains are the

cubic mixed crystals of (W,Ti,Ta)C which can be in a state of more or less perfect solid solution.

One function of TaC and (Ta,Nb)C is that of a grain growth inhibitor in hardmetals. After the initial stage of liquid phase sintering during the hardmetal production process the particles of the carbide phase begin to grow resulting in overall coarsening or isolated formation of excessively large crystals. The grain growth can be suppressed by small additions of TaC or (Ta,Nb)C. These carbides appear to interfere with the solution-reprecipitation process of WC — but the exact mechanism is not known.

The second function of TaC or (Ta,Nb)C mainly together with TiC is that of an alloying additive to WC/Co-hardmetals. By the addition of these cubic carbides a third microstructural phase besides WC and Co is formed which improves the wear resistance of hardmetals in cutting applications for long chipping materials by increasing remarkably the thermal shock resistance, hot hardness and resistance to cratering and oxidation (9).

The carbides can be added to the powder mixture for hardmetal sintering in the form of TaC (or TaC/NbC) + WC/TiC mixed crystals or as a prealloyed perfect solid solution (Triple Carbide (W,Ti,Ta)C or Quadruple Carbide (W,Ti,Ta,Nb)C) with a composition that closely corresponds to the phase composition required for a special hardmetal grade. While the first method is still the preferred one for economic reasons, the second method is to be preferred from a metallurgical standpoint and its application is growing. Prealloyed carbide mixed crystals in a perfect homogeneous solid solution improve the properties of hardmetals particularly with respect to toughness. With prealloyed mixed crystals O, N and free carbon are lower and the wettability with C is increased. There is less grain growth during sintering in the cubic carbide phase, because the diffusion process between TaC + WC/TiC mixed carbide is eliminated. The distribution in the microstructure is more homogeneous and a fine grain is easier to produce.

Ta as carbide but also as nitride is an important constituent in hard materials other than conventional hardmetals. Such hard materials based on TiC and Ti(C,N), called Cermets, should be particularly mentioned. Although the specific effects of the TaC or TaC/NbC additions in Cermets have not yet been thoroughly investigated it appears by and large that they are analogous to those in hardmetals with a Co-binder.

Much work has been carried out on the substitution of TaC in hardmetals. It was found that for most applications pure TaC can be substituted by NbC up to 30 weight % in the form of (Ta,Nb)C mixed crystals. For less stringent cutting applications or for use as grain growth inhibitor the NbC-content can be as high as about 40 weight %.

A worldwide average of TaC substitution by NbC can be estimated to be around 20 %, with Europe accounting for the highest degree of substitution of Ta by Nb. (Hf,Nb)C mixed crystals have also been found useful for uninterrupted cutting applications but have not found a wide acceptance.

During the last 15 years the hardmetal industry was very successful in keeping its raw material requirements for cutting tools more or less constant although the total chip removing volume by hardmetal inserts grew in Europe about 200 % during this period — which corresponds to an annual growth rate of about 5.6 %. This was made possible by the increasing usage of recycled hardmetal scrap, by new tool geometries and by coatings of hardmetals. This development will most probably not continue to that extent in the future. In the nineties powder consumption for cutting tools based on WC-hardmetals is expected to grow in Europe by about 2-2.5 % (10).

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